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CHEMICAL MODIFICATION OF SEMICONDUCTOR SURFACES

Final Report

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Final Report for NASA Research Grant NAG-1-89
"Chemical Modification of Semiconductor Surfaces"

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Work performed under this grant has concentrated mainly on the chemical modification of TiO_2 powders in the gas phase and the examination of the modified powders by infrared absorption spectroscopy. We sought to (1) explore the range of information obtainable by IR spectroscopy of chemically modified semiconductors, and (2) define the optimum reaction conditions for synthesizing a monolayer of methylsilanes using vapor phase reaction conditions. The results are comprehensively summarized in a paper submitted to the Journal of the American Chemical Society, a copy of which is attached. An earlier paper (copy attached) will appear in the ACS Symposium Series, "Chemically Modified Surfaces" (see below). Very briefly, we summarize the results:

(1) Silanes react rapidly in the gas phase to form an approximate monolayer on the TiO_2 surface. The silane layer is not removed by heating under vacuum (proof of bonding) or by exposure to water vapor.

(2) Coverages are virtually independent of the type of silane, reaction temperature, and vapor pressure. The silanes examined included mono- through trichloromethyl silane, mono- through trimethoxymethylsilane, and hexamethyldisilazane.

(3) Different types of surface hydroxyl groups display differing reactivities towards silanes. "Terminal" O-H groups react readily with silanes while "bridging" O-H groups remain largely unperturbed.

(4) HCl , a byproduct of the silanization with chlorosilanes, chemisorbs to the TiO_2 surface and alters it permanently. Methanol and ammonia likewise interact strongly with TiO_2 surfaces, but their effects are removed by

prolonged exposure to water vapor.

(5) IR spectroscopy is a powerful tool for studying surface modification.

We have now proceeded to the second stage: stability testing. Single crystal TiO_2 electrodes are modified with silanes in the vapor phase and examined by x-ray photoelectron spectroscopy (XPS). The electrodes are soaked in various electrolytes, or used to generate photocurrent in the same electrolytes. The Si(2p) peak is monitored (along with the O(1s), Ti(2p), and C(1s)) peaks to assess the loss of the silane. We have no firm conclusions as yet. Strong base (0.1 M NaOH) seems to strip the silane quantitatively; photocurrent generation in 0.5 M H_2SO_4 also devastates the silane layer. These results are tentative. The x-ray photoelectron spectrometer suffers from varying sensitivity and frequent breakdowns. Also, the Si(2p) peak conveys no information as to the chemical nature of the silicon. Consequently, we are exploring alternate methods, preferably vibrational spectroscopies, for examining silane monolayers on single crystal electrodes.

The work described above has been done principally by one Ph.D. candidate, R. S. Vithanage. Assistance was provided by several undergraduates: Albert Wagner (summer, 1980); Barry Flannagan (spring and fall, 1981); and Martha Gilliam (summer, 1981). A new graduate student, Jim Cwynar, will start work soon on GaAs. We plan to duplicate the IR study done on TiO_2 and to attempt to passivate the GaAs photoelectrochemical oxidation.

Presentations

1. Talk. "Infrared Absorption Spectroscopy of Chemically Modified Semiconductors: TiO_2 and Me_3SiCl ", H. O. Finklea, open session at the Gordon Conference on Electrochemistry, Ventura, CA, Jan. 1981.

2. Poster. "Chemical Modification of TiO_2 with Methylsilanes and Characterization by Infrared Absorption Spectroscopy", H. O. Finklea and R. S. Vithanage, American Chemical Society 182nd National Meeting, New York, NY, Aug. 1981, Abstract # INOR 119.
3. Talk. "Infrared Absorption Studies of Chemically Modified TiO_2 : Reactions with Methylsilanes", H. O. Finklea and R. S. Vithanage, The Electrochemical Society 160th National Meeting, Denver, CO, Oct. 1981, Abstract # 564.

Papers

1. Finklea, H. O., and R. Vithanage. "Chemical Modification of TiO_2 Surfaces with Methylsilanes and Characterization by Infrared Absorption Spectroscopy", Chemically Modified Surfaces, ACS Symposium Series, ed. J. S. Miller. Accepted.
2. Finklea, H. O., and R. S. Vithanage. "Infrared Absorption Spectroscopy of Chemically Modified Titanium Dioxide", submitted to the Journal of the American Chemical Society.

Grant Proposal

"Chemical Modification of Semiconductor Surfaces with Non-electroactive Molecules". \$228,276 requested for three years. Submitted to Department of Energy, Army Research Office, Office of Naval Research, and Air Force Office of Scientific Research.